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Component Ratio Effect of Melamine Cyanurate/Magnesium Hydroxide on the Flame-retardant Properties of Ethylene-Propylene-diene Terpolymer Rubber

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Abstract

A synergistic flame-retardant compound containing magnesium hydroxide (MH) and melamine cyanurate (MCA) ingredients was prepared with ethylene-propylene-diene monomer (EPDM) composite to find a highly efficient, halogen-free, and phosphorus-free flame retardant. The flame-retardant MH/MCA compound particles were modified by a silane coupling agent to increase surface activity. Two series of EPDM/MH/MCA composites were prepared by direct blending methods. The mechanical and flame-retardant properties of the composites were investigated by various methods. The Rockwell hardness and tensile strength of EPDM/MH/MCA composites significantly increased after adding MH/MCA compound particles compared with EPDM composites. Results showed that incorporating MH/MCA compound particles evidently improved the flame-retardant and mechanical properties of EPDM. Both of these properties increased, and the flame-retardant properties of the materials met the UL94 V-1 requirements. The excellent properties of the composites were obtained after adding 40 phr MH and 20 phr MCA with a silicane coupling agent. Results indicated that the EPDM/MH/MCA composite with the appropriate MH/MCA mass ratio had the highest LOI, UL94 V-0 rating, lowest heat release rate, and highest residue yield. These results implied that the appropriate MH/MCA mass ratio formed a better flame-retardant system and adequately exerted their synergistic effects. Different flame-retardant performances should be attributed to their own characteristics, dispersion state in EPDM matrix, and the change of structure during burning.

Keywords

Additives; Elastomers; Flame Retardance; Blending; Rubber

Introduction

Ethylene-propylene-diene monomer (EPDM) rubber is widely used in many areas, such as rubber, wire, cable industry, and building materials, because of its unique properties, such as high aging resistance, weather resistance, chemical resistance, ozone resistance, excellent insulating properties, and flexibility at low temperature [1-2]. However, EPDM is extremely flammable, which restricts its application in many fields and leaves security risk without adequate flame-retardant treatment [3-4]. Therefore, developing flame-retardant EPDM composites has been the focus of research in recent years [3, 5-6]. Considerable research has been conducted on the flame retardancy of EPDM-based blends instead of the neat EPDM [7-9]. Research on flame-retardant EPDM blends mainly uses halogenated additives, such as decabromodiphenyl oxide, associated with antimony trioxide [10-11]. Halogen-antimony synergistic system is speculated as an effective fire-retardant method for most EPDM composites [12-13]. However, its future is confronted with extreme pressure from environmental concerns because of the evolution of toxic gases and corrosive chemical fumes from combustion or pyrolysis, which can choke people exposed to the fumes and damage costly equipment. Because of environmental and health considerations, developing effective halogen-free flame retardants and relevant flame-retardant materials has recently become a popular topic [14-15].

Incorporating halogen-free flame retardants, such as metal hydroxides, mainly magnesium hydroxide (MH) and aluminum trihydrate, into EPDM is a common way to improve the flame-retardant property of materials [16-17]. Metal hydroxides are widely used as environment-friendly flame retardants because of their low toxicity, anticorrosion properties, low cost, and low smoke emission during processing and burning[14,16, 18]. The flame-retardant mechanism of this filler is speculated to be achieved through a physical effect caused by endothermic decomposition, where the release of water vapor dilutes the fuel supply and cools the matrix, and the degradation products work as a barrier [14, 18]. However, the high loading (>50% by weight) required for adequate flame retardancy often leads to a marked deterioration in the mechanical properties of the materials. Nitrogen-containing flame retardants have recently attracted considerable research interest [19-20]. Environment-friendly melamine cyanurate (MCA) possesses excellent mechanical properties, good thermal stability, low toxicity, low corrosion resistance, and good compatibility with the environment and thus has great potential application in flame retardants [19, 21-22]. Compared with halogen- or phosphorus-containing flame retardants, MCA with lower toxicity and flame retardancy has excellent comprehensive performance, which enables the flame-retardant materials to achieve the UL94 level [23-26]. Therefore, investigating the flame retardancy of EPDM by introducing new methods and technology is an important and urgent task.

In this study, we designed a novel synergistic flame-retardant compound by integrating the MH and MCA ingredients with very effective flame retardancy. The flame-retardant particles were modified by a silane coupling agent to increase surface activity. Two series of EPDM/MH/MCA composites were prepared by direct blending methods, and the effect of MH/MCA compound particles on the flame-retardant and mechanical properties of EPDM composites was evaluated. The flame-retardant properties were investigated by vertical combustion performance. This study mainly aimed to develop a new type of low-smoke, halogen-free, phosphorus-free, and nitrogen-containing flame retardant to be applied on the EPDM rubber. The results can provide the best process conditions and technical reference. EPDM composites with good flame-retardant and mechanical properties were obtained. Furthermore, the difference between the synergistic effects of MH and MCA on the flame retardancy of EPDM was comprehensively investigated. To our knowledge, this study is the first to investigate the synergistic flame-retardant effects of MH and MCA on the flame retardancy of EPDM.

Experimental

Materials

EPDM containing 73.0 wt.% ethylene and 5.0 wt.% ethylidene norbornene was supplied by China Petroleum & Chemical Corporation. MH was bought from Schennor Science and Technology Co., Ltd. China and was used as received. MCA was supplied by Shanghai Chlor-alkali, China. The average particle size was 50 nm. MCA was used without further treatment. Silicane coupling agents (Si-69) were purchased from Nanjing Shuguang Chemical Group Co., Ltd. (China).

Sample Preparation

Before functionalization, pristine MH and MCA powders were dried in a vacuum oven at 120.0 °C for 24 h to remove the adsorbed moisture from their surface. A total of 60 g of the MH/MCA compound particles were accurately weighed and added into the flask. Pristine MH or MCA particles (according to a certain proportion) were then dispersed in 150.0 mL of ethyl acetate with ultrasonic agitation, and a certain amount of coupling agent (3.0 wt.% of particles) was added into the flask. The reaction was refluxed at 75.0 °C for 3.5 h with agitation. The product was then filtered and washed using ethyl acetate and dried at 110 °C for 24 h in a vacuum oven.

To examine the efficiency of different flame-retardant additives, 11 sample formulations were prepared with different concentrations (TABLE 1). Five sample formulations were prepared by incorporating MH and MCA (45:15, 40:20, 30:30, 20:40, and 15:45 wt.% of each) in the ternary blend of EPDM/MH/MCA and designated as S1, S2, S3, S4, and S5, respectively. The other five sample formulations were prepared by silane coupling agents (Si-69) in the ternary blend of EPDM/MH/MCA and designated as S6, S7, S8, S9, and S10, respectively. The pure EPDM was processed in an open mill at 90 °C for 5 min, and then the additives were added in the order of zinc oxide, stearic

acid, and sulfurizing agent. Then, they were cured in a platen press under 1 MPa pressure at 160 ± 1 °C for 40 min and removed from the plate vulcanizing machine. The compression-molded sheet was conditioned at 40 °C to 50 °C for 24 h and used to prepare the specimens for test and evaluation.

TABLE 1 COMPOSITION OF VARIOUS SAMPLES

Sample code	EPDM (phr)	MH (phr)	MCA (phr)	Sample code	EPDM (phr)	MH (phr)	MCA (phr)	Si-69 (phr)
S0	100	0	0	-	-	-	-	-
S1	100	45	15	S6	100	45	15	1.9
S2	100	40	20	S7	100	40	20	1.9
S3	100	30	30	S8	100	30	30	1.9
S4	100	20	40	S9	100	20	40	1.9
S5	100	15	45	S10	100	15	45	1.9

Characterization and Measurement

The Rockwell hardness test was carried out according to ISO 868 standard. Tensile properties were measured following GB/T 528-1998 using a TCS Universal testing machine model 2000. The specimens were evaluated at a crosshead speed of 5 mm/min up to stress yield and then 50 mm/min until failure. Tests were performed in duplicate up to three times, depending on whether the deviation between the results was <10%.

The flame retardancy of all prepared samples was evaluated by limiting oxygen index (LOI) and UL94 tests. The LOI values are measured on an oxygen index instrument (HC-2, Jiangning Analysis Instrument Factory, China) according to ASTM D2863. Test specimens of dimensions 100 mm×6.5 mm×3mm were cut from pressed plates. Better flame retardancy is represented by higher LOI values.

UL-94 vertical burning tests, performed on integrated vertical testing apparatus (CZF-3, Jiangning Analysis Instrument Factory, China), were performed with samples of dimensions 130 mm×13 mm×3mm. The classifications are defined according to the American National Standard UL-94. The test methods are generally reproducible to an accuracy of ±0.5%.

Results and Discussion

Mechanical Properties Studies

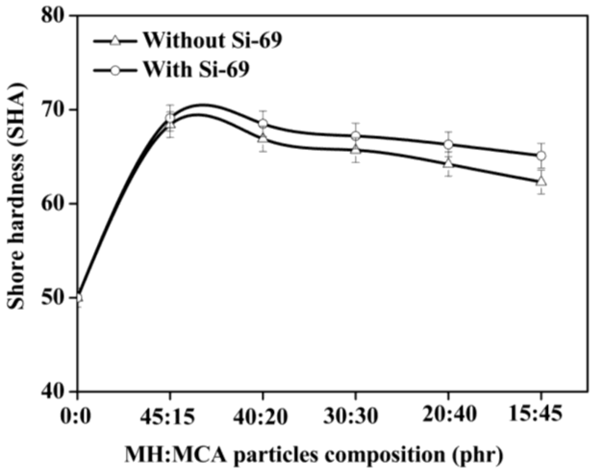

FIG. 1 ROCKWELL HARDNESS VARIATION OF THE MH AND MCA COMPOUND PARTICLE COMPOSITIO

Considering practical industry requirements, investigating the effect of the flame retardants on the mechanical property of EPDM is necessary. Fig.1 shows that introducing MH/MCA compound particles into EPDM composites resulted in increased Rockwell hardness. The Rockwell hardness of pure EPDM was very poor without any added filler. Compared with the pure EPDM, the Rockwell hardness of EPDM/MH/MCA composites significantly increased after adding MH/MCA compound particles. The Rockwell hardness of EPDM composites

increased with MH and MCA composition variation when 45 phr MH and 15 phr MCA particles were filled in the EPDM materials, and then decreased with the increase of MCA composition. The increased hardness was caused by the enhanced interaction between MH/MCA compound particles and the matrix because of the large specific surface area of the composite particles. This characteristic is very important for the practical usage of EPDM as cable materials and so on. The Rockwell hardness of EPDM composites with a silicane coupling agent significantly increased compared with EPDM composites without a silicane coupling agent. This result is mainly attributed to the increased dispersion of such fillers with an Si-69 coupling agent in the matrix, which possibly influenced the hardness by decreasing the chain mobility of EPDM. These fillers may also act as physical cross-linking points to provide a positive effect on the reinforcement of the Rockwell hardness, especially for MH[14,16-17].

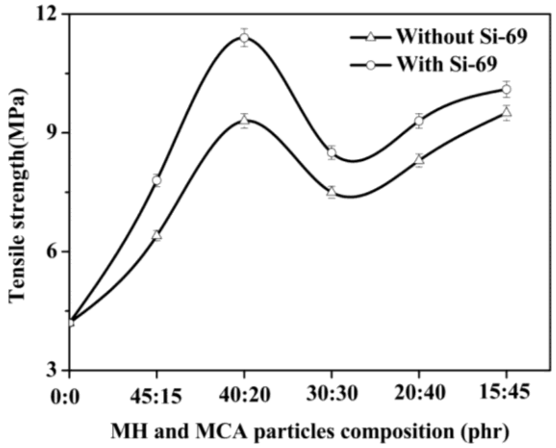

FIG. 2 TENSILE STRENGTH VARIATION OF THE MH AND MCA COMPOUND PARTICLE COMPOSITION.

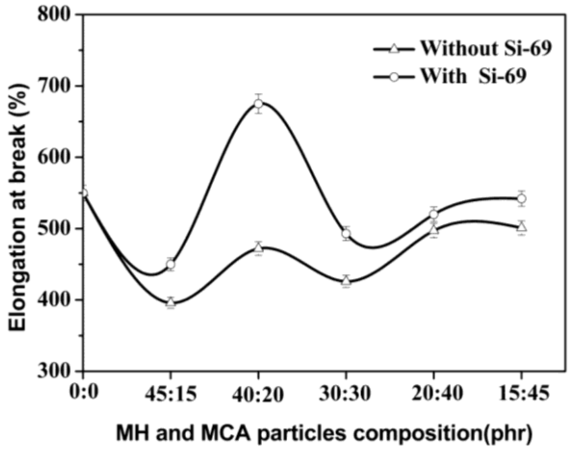

FIG. 3 ELONGATION AT BREAK VARIATION OF THE MH AND MCA COMPOUND PARTICLE COMPOSITION

The influence of the flame-retardant content on the tensile properties of EPDM flame-retardant samples is shown in Fig.2 and Fig.3. The tensile properties of pure EPDM without any filler added were very poor, especially the tensile strength (4.20 MPa). A noticeable improvement of the tensile strength was observed after adding MH and MCA particles, but the elongation at break of EPMD decreased. The tensile strength and elongation at break of the composites achieved a maximum value when the composition of MH and MCA was 40 and 20 phr, respectively. This result is mainly due to the direct effect of MH material on the mechanical properties. After the scattered addition of MH to the EPDM, the distribution of flame retardants and EPDM led to improved size performance. The compound interfacial bonding force between flame retardants and EPDM, which was enhanced after the surface modification of MH/MCA in the EPDM mixing process, led to improved tensile strength and elongation at a certain extent. Compared with EPDM/MH/MCA material without a coupling agent, the tensile strength and elongation at break of EPDM/MH/MCA compound activated by a silane coupling agent (Si-69) increased with the same composition of flame retardant. On the one hand, the dispersion properties of such fillers in the matrix significantly reduced the powder surface free energy, improved hydrophobicity, increased surface active group, improved the wettability and interaction with EPDM, improved the dispersion of MH and MCA particles in EPDM,

and improved the performance of the rubber[16-17,19]. On the other hand, these fillers may act as physical cross-linking points to provide a positive effect on the reinforcement of the mechanical property. Meanwhile, the force between MH and MCA with surface modification and EPDM increased in the EPDM mixing process, leading to improved hardness and tensile properties of the composites at a certain extent. The hardness and tensile properties of EPDM composites with an Si-69 coupling agent activation showed the best result when the filler composition of MH and MCA is 40 and 20 phr, respectively (Fig. 2 and Fig.3). This result is mainly due to the MH and MCA particles with a silane coupling agent, which may have synergistic flame-retardant effects as physical cross-linking points to provide a positive effect on the reinforcement of the mechanical property.

Flammability Studies

TABLE 2 RESULTS OF THE UL94 VERTICAL BURNING TEST FOR EPDM COMPOSITES

code	Self-extinguishing time (s)	Dripping	Smoke	UL 94 rating
S0	failed	Yes	Yes	No rating
S1	16.3	No	No	V-1
S2	10.9	No	No	V-1
S3	20.6	No	No	V-1
S4	22.3	No	No	V-1
S5	29.4	No	No	V-1
S6	12.8	No	No	V-1
S7	7.9	No	No	V-0
S8	18.5	No	No	V-1
S9	21.8	No	No	V-1
S10	25.1	No	No	V-1

To evaluate the flame retardancy of polymeric materials, we tested the limited oxygen index (LOI) value of various composites with MH and MCA particles (Fig. 4). The experimental results revealed that pure EPDM was easily flammable with an extremely low LOI value of 19.5% and could not pass the UL94 test. The flame retardancy of EPDM/MH/MCA composites could be effectively improved with a certain loading of MH or MCA as synergistic additives. The LOI values increased with the introduction of MH until a maximum value was reached; then, the values began to decrease as the content of MH further increased. The highest LOI value in EPDM/MH/MCA composites was 28.0% when 40 phr MH and 20 phr MCA particles were incorporated. The LOI value of EPDM composites with Si-69 increased compared with EPDM composites without an Si-69 coupling agent. The highest LOI value of EPDM/MH/MCA composites with an Si-69 coupling agent was 30.0% as 45 phr MH and 15 phr MCA particles were compounded.

The UL94 rating is the most widely used as plastic material inflammable performance standard in evaluating the extinguishing ability. In the UL94 test, the self-extinguishing time is one of the important evaluation indices for flame-retardant properties. The shorter self-extinguishing time indicates that the flame-retardant materials are more difficult to burn and have better fire-retardant properties. Table 2 shows the results of the UL94 vertical burning test for EPDM composites.

As shown in Table 2, the experimental results revealed that the pure EPDM was easily flammable with an extremely low LOI value and could not pass the UL94 test. EPDM burns after ignition and exhibits dripping and smoke. Adding MH/MCA composite flame retardant could obviously increase the flame-retardant classification for the EPDM composite. The addition of MH/MCA compound particles to EPDM significantly modified the process of burning. As the amount of MH compositions increased further to 40 phr, the self-extinguishing time quickly decreased, even becoming better than those of the pure EPDM; the combustion level gradually reached level V-1, and the flame-retardant properties evidently improved after adding the flame-retardant MH/MCA compound. For the EPDM composites with 40 phr MH and 20 phr MCA compound particles, the self-extinguishing time reached 10.9 s, whereas that of S1 sample reached 16.3 s using 45 phr MH and 15 phr MCA compound particles. The dripping tendency during EPDM composite combustion became weaker compared with EPDM. Adding MH/MCA compound particles for EPDM composites leads to improved flame-retardant properties. The flame retardancy

mechanism of MH particles is based on its thermal decomposition between 200 and 400 °C. During this energy-consuming process or endothermic reaction, MH released its chemically bonded water (34.6 wt.%), while the corresponding magnesium oxide remained as char residue. During thermal decomposition, MH releases moisture, absorbs a large number of latent heat, reduces the actual temperature of the flame on the material surface, reduces the speed of polymer degradation, reduces the fuel production, releases water vapor by reducing the surface of the oxygen concentration, and makes surface burning more difficult. MH can delay ignition time and reduce smoke quantity and escape velocity because of catalytic oxidation. The MCA mechanism is a gas-phase flame retardant in EPDM. During EPDM combustion, MCA easily sublimates, which absorbs and takes away a lot of heat [20-21]. Meanwhile, the thermal decomposition temperature of the nitrogen flame retardant is higher. After thermal decomposition, releasing ammonia, nitrogen, nitrogen oxides, water vapor, and nonflammable inert gas is easy. Inert gas generation and flame-retardant volatility or decomposition consumes a lot of heat and greatly reduces the surface temperature of the polymer. Inert gas not only can reduce oxygen concentration in the air and combustible volatiles but can also form an effective separation between flaming and unfired layers, which restrain flame, slow intense combustion, and gradual self-extinguishing, resulting in improved flame-retardant properties. Part of the flame-retardant gases, such as ammonia, can still react with oxygen in air to produce nitrogen gas, water, and high oxide, consume oxygen on the polymer surface, and at the same time lead to a favorable flame-retardant effect[14,16-17, 19-20]. Two kinds of flame retardants improved the performance of the flame-retardant EPDM at a certain extent.

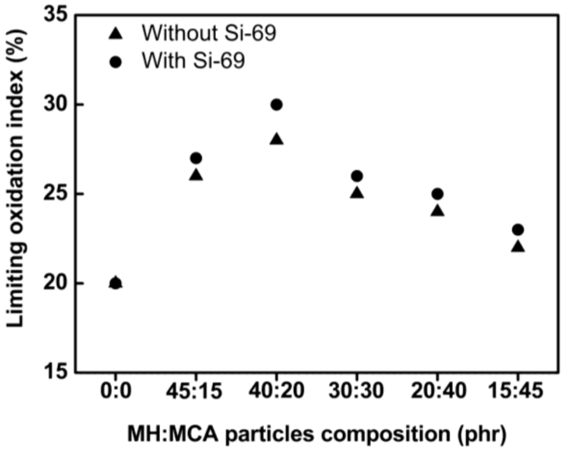

FIG. 4 EFFECT OF MH AND MCA PARTICLES ON THE LOI OF THE COMPOSITES

Under the same proportion, the self-extinguishing time of flame-retardant EPDM composites with an Si-69 coupling agent was short, which showed the improved flame-retardant properties, compared with EPMD/MH/MCA without an Si-69 coupling agent. Apparently, the UL94 vertical burning rates of the specimens increased with increasing dosage of flame-retardant MH. In the UL94 test, the EPDM/MH/MCA composite could reach a V-0 rating, indicating that MH/MCA compound particles exhibited a better synergistic performance. These MH/MCA fillers may act as physical cross-linking points to provide a positive effect on the reinforcement of the flame-retardant property. At the same time, the force between MH and MCA with surface modification and EPDM increased in the EPDM mixing process, leading to improved flame-retardant properties of composites at a certain extent. The MH and MCA flame-retardant compound with an Si-69 coupling agent exhibited synergistic flame-retardant properties, thus indicating effective improvement in properties. The best mechanical and flame-retardant properties of EPDM could be reached after adding 40 phr MH and 20 phr MCA compound particles.

Conclusions

To find a highly efficient, halogen-free, and phosphorus-free flame retardant, we prepared a novel synergistic flame-retardant compound containing MH and MCA with EPDM composite. The flame-retardant compound particles were modified by a silane coupling agent to increase surface activity. The Rockwell hardness and tensile strength of EPDM/MH/MCA composites significantly increased after adding MH/MCA compound particles. The mechanical properties of EPDM composites increased with MH and MCA composition variation when 45 phr MH and 15 phr MCA particles were filled in EPDM and then decreased with increasing MCA composition. The results

showed that incorporating MH/MCA compound particles evidently improved the flame-retardant and mechanical properties of EPDM. Specifically, incorporating 40 phr MH and 20 phr MCA with a silicane coupling agent showed the highest LOI value, and EPDM/MH/MCA with Si-69 exhibited the best UL94 vertical burning result as well as the best tensile performance among all samples. The EPDM/MH/MCA composite could reach a V-0 rating, indicating that MH/MCA compound particles exhibited a better synergistic performance.

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